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SYNTHESIS OF SUBSTITUTED ARYLOXYPHTHALONITRILES BASED ON 4-CHLOROPHTHALONITRILE AND 4,5-DICHLOROPHTHALONITRILE

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4-chlorophthalonitrile, 4,5-dichlorophthalonitrile, activated aromatic nucleophilic substitution, substituted aryloxyphthalonitriles, arylendioxydiphthalonitriles, dibenzo[1,4]dioxin

Abstract. *We obtained mono- and bis(aryloxy)phthalonitriles as well as 6-membered heterocyclic dibenzo[1,4]dioxin systems on the basis of the activated aromatic nucleophilic substitution reaction between 4-chlorophthalonitrile, 4,5-dichlorophthalonitrile and mono- and bisphenols containing different substituent not described in the literature before.*

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Substitution of halogen atom or nitro group of activated aromatic systems is still a convenient way to obtain a wide range of polyfunctional compounds, promising for use in various fields of science and technology [1-6]. Alkyl-, aryl-, araloxy-, heteryl-, and other substituted mono- and diphthalonitriles synthesised by the above mentioned S_NAr-reactions take their proper place in this range. The scientific literature presents many ways of producing different types of *ortho*-dicarbonitriles based on 4-nitrophthalonitrile [3, 7-9], 4-bromo-5-nitrophthalonitrile [9-13], tetra- and dichlorophthalonitrile [14, 15] as well as options for their practical application and various industries. These include the development of new biologically and pharmacologically active drugs [16-19], effective phthalocyanine dyes [20-22], and polyetherimides [3, 23-25].

This paper discusses the potential of this reaction used to produce new and some already known compounds (Fig. 1).

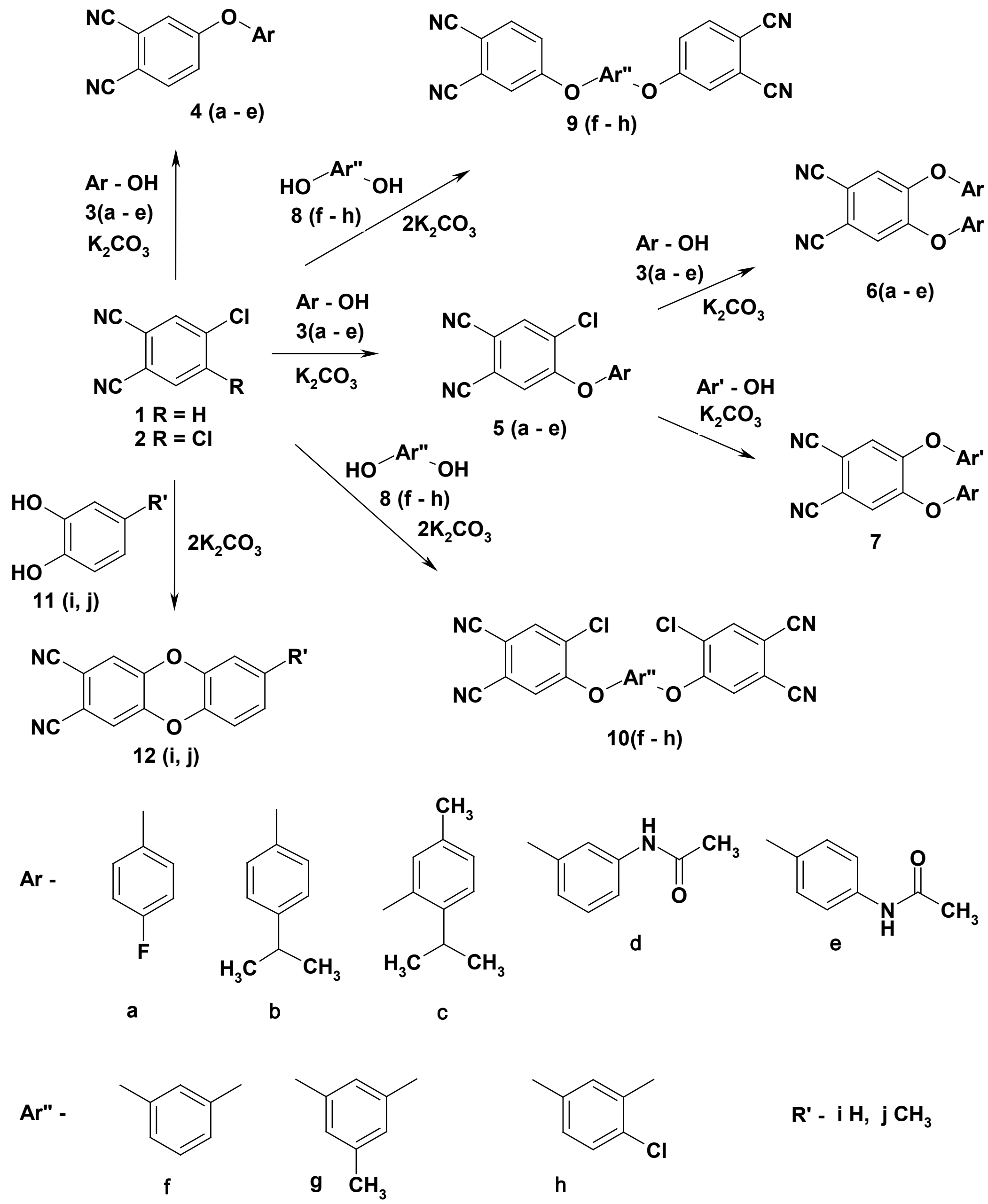

Fig. 1.

We use 4-chlorophthalonitrile (4-CPHN) **1** and 4,5-dichlorophthalonitrile (4,5-DCPH) **2**, aromatic systems containing two electron acceptor cyanogroups in the benzene ring, activating one or two chlorine atoms for S_NAr-reactions by mono- and bifunctional *O*-nucleophiles as initial key substrates.

The presence of electron acceptor substituents (especially cyanogroups) in the mentioned substrates **1**, **2** significantly decreases the electron density in the benzene ring in full accordance with the known mechanism [1]. It allows proton-donating nucleophiles formed in the reaction mixture to successfully attack the carbon atoms bound to the chlorine atoms (nucleofuges), which consequently leads to the formation of relatively stable intermediates. The formation of new and thermodynamically advantageous structure of aryloxyphthalonitrile (**4**, **5**), 4,5-bis(aryloxy)phthalonitrile (**6**, **7**), arylendioxydiphthalonitrile (**9**, **10**) is a logical result of this process.

We have implemented two approaches for the above mentioned S_NAr reactions with chlorophthalonitriles **1**, **2** - heterophase and homophase. The classical heterophase method is good with weakly activated substrates, as has been proven in practice. We obtained the best results by interaction of 4-CPHN **1** with phenols **3** **(a-e)** and bisphenols **8** **(f-h)** under intensive stirring and heating the reaction mixture in anhydrous DMFA at the presence of finely dispersed calcined potassium carbonate. The heterophase method should also be used to obtain the symmetrical and asymmetrical **6(a-e)** and **7** disubstitution products in 4,5-DCPH. This is because the 4-aryloxy-5-chlorophthalonitriles **5** **(a-e)** synthesised contain a chlorine atom which is still capable of participating in the S_NAr reaction, but at higher temperature. The use of phenols with a large number of electron-donating substituents in the benzene ring or thiophenols will also promote these reactions.

In order to obtain mono-substitution products **5(a-e)** based on 4,5-DCPH **2,** it is reasonable to use homophase method and conduct the reaction using binary solvent DMFA-H_2O. In this case, we used K_2CO_3 as the deprotonating agent providing the *in situ* generation of the reactive *O*-nucleophilic complex, as the most available and a comparatively rapid process. The use of the homophase method makes it possible to obtain 4-aryloxy-5-chlorophthalonitriles **5(a-e)** with good yields without the impurities of the disintegration products, due to the formation of little soluble in aqueous DMFA and precipitated out of the reaction mixture target products, which did not require additional purification.

If pyrocatechines **11** **(i**, j) containing two hydroxyl groups in *ortho*-position were used as starting bisphenols for the considered interaction with 4,5-DCPH 2, sequential intermolecular and then intramolecular reactions of halogen atom substitution by bifunctional *O*-nucleophile resulted in formation of heterocyclic dibenzodioxin system containing two cyanogroups **12 (i**, **j)**.

Thus, using 4-CPHN, 4,5-DCPH and various mono- and bifunctional *O*-nucleophiles, the synthesis of 4-aryloxy-5-chlorophthalonitriles not considered in literature and a wide range of already known *ortho*-dicarbonitriles containing different substituents becomes possible.

Experimental part

We recorded the IR spectra on a Perkin Elmer RX-1 FT-IR spectrometer at 700-4000 cm^{-1} (suspended in Vaseline oil).

We recorded ^1H NMR spectra on a Bruker DRX-500 device for 5% solutions of samples in DMSO-d^6 at 30 °C. We used the residual solvent proton signals in proton spectra ($\delta\delta_H$ 2.50 ppm.) or DMSO-d^6 signal in carbon spectra ($\delta\delta_C$ 39.5 ppm.) as a reference for the chemical shift reference.

We performed elemental analyses on a "Hewlett-Packard HP-85B" C, H, N analyser.

We obtained **4-CPHN 1 4,5-DCPH 2** from commercially available 4-chlorophthalic and 4,5-dichlorophthalic acids by the methodology similar to that presented in [13].

Phenols, bisphenols as well as other reagents and solvents are commercially available.

4-(Aryloxy)phthalonitriles 4 **(a-e)** (common methodology). We filled 1.73 g (0.01 mol) of 4-CPHN **1**, (0.01 phenol **3** **(a-e)),** 1.56 g (0.01 mol) of K_2CO_3 and 30 cm^3 of DMFA into a flask equipped with stirrer, reflux condenser, and thermometer under TLC monitoring. We stirred the reaction mixture intensively at 90-95 °C for 2.5-3.0 hours under TLC monitoring. At the end of the reaction, we cooled the reaction mixture to 5-10 °C and poured it into 100 cm^3 of cold water. We filtered off the resulting precipitate, washed with water (3× 50 cm^3) and dried at 70 °C. We obtained the target products **4 (a-e)** with a yield of 74-93% according to the theory.

4-Aryloxy-5-chlorophthalonitriles 5 (a-e) (common methodology). We filled 0.01 mole of 4,5-DCPH **2**, 0.01 mole of phenol **3 (a-e)** and 30 cm^3 of DMFA into a flask equipped with stirrer, reflux condenser, and thermometer. We added to the reaction mixture a solution of 1.56 g (0.01 mol) of K_2CO_3 in 10 cm^3 of water after dissolving the reagents under vigorous stirring. We stirred the reaction mixture intensively at 90-95 °C for 1-2 hours under TLC monitoring. At the end of the reaction, we cooled the reaction mixture to 5-10 °C and poured it into 100 cm^3 of cold water. We filtered off the precipitate, washed with 2-propanol (50 cm^3), water (3× 50 cm^3) and dried at 70 °C. We obtained the monosubstitution target products **5 (a-e)** with a yield of 53-62% according to the theory.

4,5-bis(aryloxy)phthalonitriles 6 (a-e), **7.** (common methodology). We filled 0.01 mol 4-aryloxy-5-chlorophthalonitrile **5 (a-e)**, 0.01 mol phenol **3 (a-e)**, 1.56 g (0.01 mol) K_2SO_3 and 30 cm^3 DMFA into a flask equipped with stirrer, reflux condenser, and thermometer. We stirred the reaction mixture intensively at 90-95 °C for 3-5 hours under TLC monitoring. At the end of the reaction, we cooled the reaction mixture to 5-10 °C and poured it into 100 cm^3 of cold water. We filtered off the resulting precipitate of the disubstituting product, washed with water (3× 50 cm^3) and dried at 70 °C. We obtained the target compounds **6(a-e)**, **7** with a yield of (43-78) % according to the theory.

4,4'-(*m*-Arylendioxy)diphthalonitriles 9 (f-h), 10 (f-h), dibenzo[1,4]dioxin-2,3-dicarbonitriles **12 (i, j)** (common methodology). We filled 0.02 mol 4-CPHN **1** (4,5-DCPH **2**), 0.01 mol bisphenol **8 (f-h)** or **11 (i, j)**, 3.12 g (0.02 mol) K_2SO_3 and 30 cm^3 DMFA into a flask equipped with stirrer, reflux condenser and thermometer. We stirred the reaction mixture intensively at 90-98 °C for 3-5 hours under TLC monitoring. At the end of the reaction, we cooled the reaction mixture to 5-10 °C and poured it into 100 cm^3 of cold water. We filtered off the precipitate, washed with 2-propanol (50 cm^3), water (3× 50 cm^3) and dried at 70 °C. We obtained the target products **9 (f-h), 10 (f-h)** and **12 (i, j)** with a yield of 46–74% according to the theory.

4a: Yield 76%, $T_{melt.}$ = 128–130 °C. IR (υ_{max}): 2230 (CN), 1270 (C-O-C). Found, %: C, 70.52; H, 2.92; N, 11.93. $C_{14}H_7FN_2O$. Calculated, %: C, 70.59; H, 2.96; N, 11.76. NMR ^1H (400 MHz, DMSO-d_6, δ, ppm.): 7,43-7,61 (m, 5H, J=14.13 Hz), 7,7 (s, 1H), 8,14 (d, 1H, J=2.13 Hz).

4b: Yield 89%, $T_{melt.}$ = 156–157 °C. IR (υ_{max}): 2237 (CN), 1273 (C-O-C). Found, %: C, 77.80; H, 5.32; N, 10.70. $C_{17}H_{14}N_2O$. Calculated, %: C, 77,84; H, 5.38; N, 10.68. NMR ^1H (400 MHz, DMSO-d6, δ, ppm.): 1,24 (d, 3H, J=6.84 Hz), 2,91 (kv, 1H, J=6.72 Hz), 7,20-7,36 (m, 4H, J=13.01 Hz), 7,36 (d, 1H, J=8.30 Hz), 7,89 (s, 1H), 8,1 (d, 1H, J=2.10 Hz).

4c: Yield 93%, $T_{melt.}$ = 162–165 °C. IR (υ_{max}): 2230 (CN), 1259 (C-O-C). Found, %: C, 78.20; H, 5.81; N, 10,17. $C_{18}H_{16}N_2O$. Calculated, %: C 78.24; H 5.84; N 10.14. NMR ^1H (400 MHz, DMSO-d6, δ, ppm.): 1,13 (d, 6H, J=7.04 Hz), 2,23 (s, 3H), 2,91 (kv, 1H), 6,99 (s, 1H) 7,12 (d, 1H, J=8.06 Hz), 7,34 (d, 1H, J=8.06 Hz), 7,49 (d, 1H, J=6.13 Hz), 7,89 (s, 1H), 8,1 (d, 1H).

4d: Yield 74%, $T_{\text{melt.}}$ = 85–87 °C. IR ($\upsilon_{\max}$): 3262 (NH), 2237 (CN), 1668 (C=O), 1256 (C-O-C). Found, %: C, 69.22; H, 3.98; N, 15,23. $C_{16}H_{11}N_3O_2$. Calculated, %: C, 69.31; H, 4.00; N, 15.15. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,04 (s, 3H), 6,84 (d, 2H, J=9.01 Hz), 7,34 (t, 1H), 7,44 (d, 1H, J=9.12 Hz), 7,76 (s, 1H), 7,88 (s, 1H), 7,99 (d, 1H, J=7.02 Hz), 10.12 (s, 1H).

4e: Yield 88%, $T_{\text{melt.}}$ = 230–232 °C. IR ($\upsilon_{\max}$): 3264 (NH), 2234 (CN), 1664 (C=O), 1240 (C-O-C) Found, %: C, 68.76; H, 3.20; N, 17.77. $C_{18}H_{10}N_4O_2$. Calculated, %: C, 68.79; H, 3.21; N, 17.83. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,07 (s, 3H), 7,11 (m, 2H, J=9.04 Hz), 7,57 (s, 1H), 7,72 (m, 2H, J=9.14 Hz), 7,9 (s, 1H), 8,3 (d, 1H), 10,09 (s, 1H).

5a: Yield 59%, $T_{\text{melt.}}$ = 141–144 °C. IR ($\upsilon_{\max}$): 2232 (CN), 1276 (C-O-C), 1179 (C-F), 1010 (C-Cl). Found, %: C, 61.49; H, 2.25; N, 10.25. $C_{14}H_6ClFN_2O$. Calculated, % C, 61.67; H, 2.22; N, 10.27. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 7,27 (dd, 2H, J=9.28, 4.64 Hz), 7,34 (dd, 2H, 9.04, 8.55 Hz), 7,67 (s, 1H), 8,55 (s, 1H).

5b: Yield 58%, $T_{\text{melt.}}$ = 160–161 °C. IR ($\upsilon_{\max}$): 2235 (CN), 1273 (C-O-C), 1014 (C-Cl). Found, %: C, 68.77; H, 4.40; N, 9,53. $C_{17}H_{13}ClN_2O$. Calculated, % C, 68.81; H, 4.42; N, 9.44. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 1,22 (d, 6H, J=6.84 Hz), 2,94 (kv, 1H, J=6.78 Hz), 7,10 (d, 2H, J=8.06 Hz), 7,36 (d, 2H, J=8.30 Hz), 7,06 (s, 1H), 8,56 (s, 1H).

5c: Yield 53%, $T_{\text{melt.}}$ = 124–125 °C. IR ($\upsilon_{\max}$): 2235 (CN), 1276 (C-O-C), 1017 (C-Cl). Found, %: C, 69.53; H, 4.82; N, 9.09. $C_{18}H_{15}ClN_2O$. Calculated, %: C, 69.57; H, 4.86; N, 9.01. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 1,14 (d, 6H, J=7.08 Hz), 2,27 (s, 3H), 2,93 (kv, 1H), 7,12 (d, 1H, J=8.06 Hz), 7,34 (d, 1H, J=8.06 Hz), 7,45 (s, 1H), 8,55 (s, 1H).

5d: Yield 57%, $T_{\text{melt.}}$ = 191–193 °C. IR ($\upsilon_{\max}$): 3260 (NH), 2237 (CN), 1243 (C-O-C), 1020 (C-Cl). Found, %: C, 61.64; H, 3.22; N, 13,49. $C_{16}H_{10}ClN_3O_2$. Calculated, C, 61.65; H, 3.23; N, 13.48. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,02 (s, 3H), 6,89 (d, 2H, J=9.01 Hz), 7,37 (t, 1H), 7,44 (d, 1H, J=9.12 Hz), 7,66 (s, 1H), 7,88 (s, 1H), 10.12 (s, 1H).

5e: Yield 62%, $T_{\text{melt.}}$ = 223–225 °C. IR ($\upsilon_{\max}$): 3267 (NH), 2236 (CN), 1667 (C=O), 1240 (C-O-C), 1019 (C-Cl). Found, %: C, 61.59; H, 3.18; N, 13,49. $C_{16}H_{10}ClN_3O_2$. Calculated, %: C, 61.65; H, 3.23; N, 13.48. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,05 (s, 3H), 7,14 (m, 2H, J=9.04 Hz), 7,57 (s, 1H), 7,69 (m, 2H, J=9.04 Hz), 8,55 (s, 1H), 10,09 (s, 1H).

6a: Yield 49%, $T_{\text{melt.}}$ = 184–187 °C. IR ($\upsilon_{\max}$): 2232 (CN), 1220 (C-O-C), 1179 (C-F). Found, %: C, 68.99; H, 2.85; N 8.05. $C_{20}H_{10}F_2N_2O_2$. Calculated, % C, 68.97; H, 2.89; N, 8.04. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 7,27-7,43 (m, 8H, J=16.28 Hz), 7,47 (s, 2H).

6b: Yield 48%, $T_{\text{melt.}}$ = 218–220 °C. IR ($\upsilon_{\max}$): 2234 (CN), 1243 (C-O-C). Found, %: C, 78.72; H, 6.06; N, 7,03. $C_{26}H_{24}N_2O_2$. Calculated, % C, 78.76; H, 6.10; N, 7.07. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 1,22 (d, 12H, J=6.82 Hz), 2,9 (kv, 2H, J=6.71 Hz), 7,14-7,31 (m, 4H, J=8.06 Hz), 7,36 (d, 4H, J=8.30 Hz), 7,44 (s, 2H).

6c: Yield 43%, $T_{\text{melt.}}$ = 232–235 °C. IR ($\upsilon_{\max}$): 2235 (CN), 1239 (C-O-C). Found, %: C, 79.13; H, 6.62; N, 6,64. $C_{28}H_{28}N_2O_2$. Calculated, %: C, 79.22; H, 6.65; N, 6.60. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 1,14 (d, 12H, J=7.01 Hz), 2,23 (s, 6H), 2,97 (kv, 2H), 7,12-7,34 (m, 4H, J=13.1 Hz, 7,44 (d, 2H, J=3.4 Hz), 7,55 (s, 2H).

6d: Yield 67 %, 224–227 °C. IR (υ_{max}): 3260 (NH), 2237 (CN), 1664 (C=O), 1246 (C-O-C). Found, %: C, 67.54; H, 4.22; N, 13,19. $C_{24}H_{18}N_4O_4$. Calculated, %: C, 67.60; H, 4.25; N, 13.14. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,07 (s, 6H), 7,12-7,29 (m, 6H, J=10.1 Hz), 7,41 (s, 2H), 7,68 (s, 2H), 10,01 (s, 2H).

6e: Yield 78%, $T_{melt.}$ = 243–245 °C. IR (υ_{max}): 3265 (NH), 2233 (CN), 1667 (C=O), 1240 (C-O-C). Found, %: C, 67.55 9; H, 4.23; N, 13.17. $C_{24}H_{18}N_4O_4$. Calculated, %: C, 67.60; H, 4.25; N, 13.14. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,03 (s, 6H), 7,14-7,19 (m, 4H, J=9.04 Hz), 7,41 (d, 4H, J=3.1 Hz), 7,71 (s, 2H), 10,01 (s, 2H).

9f: Yield 68%, $T_{melt.}$ = 185–187 °C. IR (υ_{max}): 2235 (CN), 1275 (C-O-C). Found, %: C, 72.86; H. 2.77; N, 15.47. $C_{22}H_{10}N_4O_2$. Calculated, %: C, 72.92; H, 2.78; N, 15.46. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 6,80 (s, 1H), 7,15 (d, 2H, J=2,69 Hz), 7,29-7,43 (m, 3H, J=10.18 Hz), 7,95-8,30 (m, 4H, J=16,3 Hz).

9g: Yield 74%, $T_{melt.}$ = 191–192 °C. IR (υ_{max}): 2234 (CN), 1274 (C-O-C). Found, %: C 73.35; H, 3.15; N, 14,85. $C_{23}H_{12}N_4O_2$. Calculated, %: C, 73.40; H, 3.21; N, 14.89. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,3 (s, 3H), 6,7 (s, 1H), 7,0 (s, 2H), 7,31-7,59 (m, 2H, J=10.2 Hz), 7,95-8,24 (m, 4H, J=14,3 Hz).

9h: Yield 67%, $T_{melt.}$ = 208–211 °C. IR (υ_{max}): 2233 (CN), 1244 (C-O-C), 1060 (C-Cl). Found, %: C, 66.54; H, 2.28; N, 14,16. $C_{22}H_9ClN_4O_2$. Calculated, %: C, 66.59; H, 2.29; N, 14.12. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 7,56 (dd, 1H, J=8.67, 2.56 Hz), 7,62 (dd, 1H, J=8.79, 2.69 Hz), 7,79 (d, 1H, J=8.79 Hz), 7,95 (dd, 2H, J=5.86, 2.69 Hz), 8,10-8.16 (m, 2H).

10f: Yield 58%, $T_{melt.}$ = 189–191 °C. IR (υ_{max}): 2235 (CN), 1275 (C-O-C), 1015 (C-Cl). Found, %: C, 61.26; H, 1.86; N, 12,97. $C_{22}H_8Cl_2N_4O_2$. Calculated, %: C, 61.27; H, 1.87; N, 12.99. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 7,10 (s, 1H), 7,15 (dd, 2H, J=8.30, 2.20 Hz), 7,61 (t, 1H, J=8.18 Hz), 7,95 (s, 2H), 8,55-8.58 (m, 2H).

10g: Yield 54%, $T_{melt.}$ = 194–196 °C. IR (υ_{max}, oil): 2234 (CN), 1274 (C-O-C), 1012 (C-Cl). Found, %: C, 61.95; H, 2.25; N 12,63. $C_{23}H_{10}Cl_2N_4O_2$. Calculated, %: C, 62.04; H, 2.26; N, 12.58. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2,3 (s, 3H), 7,13 (s, 1H), 7,2 (s, 1H), 7,61 (s, 1H), 7,9 (s, 1H), 8,4 (s, 1H), 8,59-8,64 (m, 2H).

10h: Yield 57%, $T_{melt.}$ = 201–204 °C. IR (υ_{max}): 2235 (CN), 1263 (C-O-C), 1012 (C-Cl). Found, %: C, 56.72; H, 1.50; N, 12,06. $C_{22}H_7Cl_3N_4O_2$. Calculated, %: C, 56.74; H, 1.52; N, 12.03. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 7,29 (dd, 1H, J=8.91, 2.81 Hz), 7,45 (d, 1H, J=2.69 Hz), 7,84 (d, 1H, J=8.79 Hz), 7,94 (s, 1H), 8,01 (s, 1H), 8,57 (d, 2H, J=8.79 Hz).

12i: Yield 54%, $T_{melt.}$ = >300 ^{o}C. IR (υ_{max}): 2230 (CN), 1250 (C-O-C). Found, %: C, 71.72; H, 2.60; N, 11,98. $C_{14}H_6N_2O_2$. Calculated, %: C 71.79; H, 2.58; N 11.96. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 6, 85-7.00 (m, 4H, J=25 Hz), 7.70 (s, 2H).

12j: Yield 46%, $T_{melt.}$ = 237–239 ^{o}C. IR (υ_{max}): 2238 (CN), 1250 (C-O-C) Found, %: C, 72.55; H, 3.22; N 11,26. $C_{15}H_8N_2O_2$. Calculated, %: C, 72.58; H, 3.25; N, 11.28. NMR ^{1}H (400 MHz, DMSO-d6, δ, ppm.): 2.23 (s, 3H), 6.85 (m, 2H, J=3.02 Hz), 6.94 (s, 1 H), 7.8 (s, 2 H).

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